(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 814 524 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
29.12.1997 Bulletin 1997/52

(51) Int. Cl.⁶: H01M 4/50, C01G 45/02

(21) Application number: 97109043.6

(22) Date of filing: 04.06.1997

(84) Designated Contracting States:
AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE

(30) Priority: 17.06.1996 JP 155677/96
29.08.1996 JP 228794/96
03.12.1996 JP 322967/96
09.04.1997 JP 90805/97

(71) Applicant:
MURATA MANUFACTURING CO., LTD.
Nagaokakyo-shi Kyoto-fu 226 (JP)

(72) Inventors:
- Hattori, Koji
Nagaokakyo-shi, Kyoto-fu (JP)
- Yamashita, Yasuhisa
Nagaokakyo-shi, Kyoto-fu (JP)

(74) Representative:
Zinnecker, Armin, Dipl.-Ing. et al
Lorenz-Seidler-Gossel,
Widenmayerstrasse 23
80538 München (DE)

(54) A spinel-type lithium manganese complex oxide for a cathode active material of a lithium secondary battery

(57) The invention provides a spinel-type lithium manganese complex oxide for a cathode active material of a lithium secondary battery, which is characterized in that said spinel-type lithium manganese complex oxide has an average particle diameter between 1 and 5 micrometers and a specific surface area between 2 and 10 m^2/g.

The invention also provides a process for producing the spinel-type lithium manganese compound oxide comprises the steps of 1)atomizing and pyrolyzing at least one of an aqueous solution and an alcohol solution of compounds containing metallic elements constituting a spinel-type lithium manganese complex oxide to obtain said compound oxide, and 2)annealing said spinel-type lithium manganese complex oxide to increase the average particle diameter thereof to between 1 and 5 micrometers and adjust the specific surface area thereof to between 2 and 10 m^2/g.

The spinel-type lithium manganese complex oxide which is useful as a cathode active material of a lithium secondary battery exhibits a large charge-discharge capacity and excellent charge-discharge cycle characteristics, and it can be used in a 4-V region secondary battery.

EP 0 814 524 A1

Description

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a spinel-type lithium manganese complex oxide for a cathode active material of a lithium secondary battery and a process for producing thereof. The spinel-type lithium manganese complex oxide is useful as a cathode active material of a 4-V lithium secondary battery.

Prior Art

As a method of producing a spinel-type lithium manganese complex oxide which is used as a cathode active material of a lithium secondary battery, the following methods have been proposed so far.

(a) Solid phase method in which powders of lithium carbonate and manganese dioxide are mixed with each other, and the mixture is calcined at approximately 800°C.
(b) Melt-impregnation method in which low-melting lithium nitrate or lithium hydroxide is dipped in porous manganese dioxide, and calcined.
(c) Method in which lithium nitrate and manganese nitrate are dissolved in water, and the solution is ultrasonically spray-pyrolyzed.

As a lithium manganese complex oxide which is appropriate as a cathode active material of a lithium secondary battery, the following complex oxides have been proposed.

(d) $LiMn_2O_4$ (Japanese Patent Publication No. 21,431/1996)
(e) $Li_xMn_2O_4$ in which x is $0.9 \leq x \leq 1.1$ excluding $x = 1.0$ (Japanese Patent Publication No. 21,382/1996)
(f) $Li_2Mn_4O_9$, $Li_4Mn_5O_{12}$ [J. Electrochem Soc., vol. 139, No. 2, pp. 363 - 366 (1992)]
(g) $Li_xMn_2O_y$ in which x and y are $1.0 < x < 1.6$, $4.0 < y < 4.8$, and $8/3 + (4/3)x < y < 4.0 + (1/2)x$ [Japanese Laid-Open (Kokai) No. 2,921/1996]
(h) $Li_{1+x}Mn_{2-x}O_4$ in which x is 0, 0.03, 0.05, 0.10, 0.22, 0.29 or 0.33 [Solid State Ionics 69 (1994), pp. 59 - 67]

The above-mentioned methods have, however, involved the following problems.

In the solid phase method (a), the powders of carbonate and oxide are used as starting materials, and it is, therefore, necessary to calcine the same at a relatively high temperature. Accordingly, a defective spinel such as an excess oxygen spinel tends to be formed. Further, it is impossible to uniformly mix the powders at a molecular level. For example, Li_2MnO_3 and $LiMnO_2$ are sometimes formed other than intended $LiMn_2O_4$. In order to prevent formation of such complex oxides, the calcination for a long period of time has to be repeated several times while adjusting the concentration of oxygen.

The melt-impregnation method (b) improves the uniform dispersibility of Li and Mn in comparison to the solid phase method.

However, the porous manganese material is required as a starting material. In order to obtain this porous manganese material, a milling treatment is needed. For this milling treatment, a special milling device has to be used, and impurities are incorporated through a milling medium during the milling or due to abrasion of an inner wall of the milling device, decreasing qualities of the resulting complex oxide powder as a cathode active material or increasing the cost. Further, unless the calcination is conducted for a long period of time at a low temperature to control evaporation of the low-melting lithium starting material, the crystallinity of the resulting complex oxide is decreased. Accordingly, when the complex oxide is used as an active material of a secondary battery, the crystal structure collapses during the repetition of the charge-discharge cycle of the battery, decreasing the capacity of the secondary battery. Still further, when Mn is substituted with a cation having a low valence and having an ionic radium close to that of Mn, such as Fe, Co, Ni or Mg to improve the high-rate discharge or the charge-discharge cycle characteristics of the secondary battery, it is unescapable that the distribution of Mn and the substituent cation is non-uniform in this melt-impregnation method too.

In the spray pyrolysis method (c), the elements constituting the spinel-type lithium manganese complex oxide can uniformly be mixed at the ionic level to outstandingly increase the uniformity as compared to the melt-impregnation method. Further, since the step of milling the starting materials is dispensed with, incorporation of impurities formed during the milling step can be prevented advantageously.

However, in this spray pyrolysis method, a series of steps of evaporation of the solvent and thermal-decomposition are conducted within a short period of a few seconds, with the result that the thermal history is extremely short as compared to that in the conventional calcination treatment and the crystallinity of the resulting complex oxide tends to deteriorate. Accordingly, when the complex oxide is used as an active material of a secondary battery, the crystal structure

collapses during the repetition of the charge-discharge cycle of the battery to decrease the capacity of the secondary battery. Further, since the specific surface area of the resulting complex oxide is as large as tens of centares per gram, an electrolyte in contact with this complex oxide is decomposed, sometimes notably decreasing the charge-discharge cycle characteristics and the storage properties of the secondary battery.

Still further, the compositions of the above-mentioned lithium manganese complex oxides are problematic in the following points.

When the composition (d) is used as a cathode active material of a secondary battery, the capacity of the battery is decreased to 50% of the original capacity in tens of the charge-discharge cycles.

When the composition (e) is used as a cathode active material of a secondary battery and x is $0.9 \leq x < 1.0$, the amount of the lithium ion taken out by the initial charge is decreased causing decrease of the capacity of the battery. When x is $1.0 < x \leq 1.1$, the crystal structure is changed from a cubic system of a 4-V region to a tetragonal system of a 3-V region through Jahn-Teller phase transition causing decrease of the capacity of the battery in the repetition of the charge-discharge cycle.

The composition (f) has the operating potential of approximately 3.0 V region, and therefore cannot be used as a cathode active material of a 4-V region lithium battery.

The composition (g) includes a composition close to the composition (f) of the 3-V region. In order to form these active materials, a manganese starting material having a specific surface area of from 5 to 50 m^2/g is needed. However, a powder having a large specific surface area has a strong cohesive force and cannot uniformly be mixed with a lithium starting material. It is further necessary that after the manganese and lithium starting materials are mixed, the mixture is calcined at 500°C or less for 2 hours or more and then at 850°C or less for from 1 to 50 hours. As a result, the productivity is poor.

In the composition (h), a part of a manganese site is substituted with lithium to control the Jahn-Teller phase transition and improve the cycle characteristics. Nevertheless, the mere substitution of manganese with 3.0-% lithium decreases the discharge capacity of approximately 20%.

Summary of the Invention

Accordingly, it is an object of the present invention to provide, upon solving the above-mentioned problems, a spinel-type lithium manganese complex oxide for a cathode active material of a lithium secondary battery and a process for producing thereof. The spinel-type lithium manganese complex oxide should be used as a cathode active material of a 4-V region lithium secondary battery having a large charge-discharge capacity and exhibiting excellent charge-discharge cycle characteristics, and the spinel-type lithium manganese complex oxide.

The present invention provides a spinel-type lithium manganese complex oxide for a cathode active material of a lithium secondary battery, which is characterized in that said spinel-type lithium manganese complex oxide has an average particle diameter between 1 and 5 micrometers and a specific surface area between 2 and 10 m^2/g.

In the above spinel-type lithium manganese complex oxide, said spinel-type lithium manganese complex oxide may be represented by the formula $Li(Mn_{2-x}Li_x)O_4$ wherein X is $0 \leq x \leq 0.1$ and more preferably, x is $0 < x < 0.02$.

In the above spinel-type lithium manganese complex oxide, said spinel-type lithium manganese complex oxide may represented by the formula $Li(Mn_{2-x}Li_x)O_4$ wherein x is $0 \leq x \leq 0.1$, more preferably, x is $0 < x < 0.02$, and Mn is partially substituted by Cr, Ni, Fe, Co, Mg or Li.

This described composite complex oxide solves the above mentioned problem having a high surface activity which is appropriate as a cathode active material of a lithium secondary battery.

The present invention further provides a process for producing the spinel-type lithium manganese complex oxide according to one of Claims 1 to 5, comprises the steps of: 1) atomizing and pyrolyzing at least one of an aqueous solution and an alcohol solution of compounds containing metallic salts constituting a spinel-type lithium manganese complex oxide to obtain said complex oxide, and 2)annealing said spinel-type lithium manganese complex oxide to increase the average particle diameter thereof to between 1 and 5 micrometers and adjust the specific surface area thereof to between 2 and 10 m^2/g.

In the above process, the atomizing and pyrolyzing temperature may be between 500 and 900°C and the annealing temperature may be between 600 and 850°C.

In the above process, said complex oxides containing the metallic salts may be at least one of lithium nitrate, lithium acetate and lithium formate and at least one of manganese nitrate, manganese acetate and manganese formate.

When the aqueous solution and/or the alcohol solution of the compounds containing the metallic elements constituting the spinel-type lithium manganese complex oxide is sprayed into a heating atmosphere, the pyrolysis occurs instantaneously to cause milling due to the self-chemical decomposition. Consequently, the fine complex oxide having the high surface activity can be formed. When this complex oxide is then annealed, the average particle diameter is increased to between 1 and 5 micrometers, and the specific surface area is adjusted to between 2 and 10 m^2/g. Thus, the complex oxide with the high surface activity which is appropriate as a cathode active material of a lithium secondary

battery can be obtained.

The metallic elements constituting the spinel-type lithium manganese complex oxide are Li and Mn as well as substituents for improving charge/discharge characteristics such as Cr, Ni, Fe, Co, Mg and Li [this Li is a substituent of the Mn site (octahedral site) different from Li in the tetrahedral site] to be added as required for substitution of the Mn site. Typical examples of the water-soluble compounds comprising these metal elements include an acetate, a formate, a nitrate and a chloride. These compounds are much less costly than an organic compound in which a hydrogen ion in a molecule is substituted with a metallic ion, such as an alkoxide. With these compounds, the costs of starting materials can be reduced, and this is industrially advantageous.

Thus, the process of the present invention can provide a uniform spinel-type lithium manganese complex oxide having an average particle diameter of between 1 and 5 mm and a specific surface area of between 2 and 10 m^2/g.

Accordingly, when this complex oxide, preferably the complex oxide represented by the formula $Li(Mn_{2-x}Li_x)O_4$ in which x is $0 \leq x \leq 0.1$, more preferably the complex oxide represented by the formula $Li(Mn_{2-x}Li_x)O_4$ in which x is $0 < x < 0.02$ is used as a cathode active material of a secondary battery, a lithium secondary battery which is excellent in the charge-discharge cycle characteristics and the storage characteristics can be obtained.

The present invention is illustrated specifically by referring to the following embodiments.

Brief Description of the Drawing

Fig. 1 is a sectional view illustrating an example of a lithium secondary battery.

EMBODIMENTS

First, lithium nitrate, lithium acetate, lithium formate, manganese nitrate, manganese acetate and manganese formate were prepared as compounds of metallic salts constituting a lithium manganese complex oxide. In order to obtain a lithium manganese complex oxide represented by the formula $Li(Mn_{2-x}Li_x)O_4$ (in which $0 \leq x \leq 0.1$) shown in Table 1, these compounds were then accurately weighed, and charged into a container. Then, 1,000 ml of a mixed solution of water and alcohol (volume ratio of 1:1) were added thereto, and they were dissolved therein while being stirred.

Subsequently, this mixed solution was atomized and pyrolyzed at a rate of 1,200 ml/hr from a nozzle to a vertical-type caramic tube reactor adjusted to a predetermined temperature of from 400 to 900°C to obtain a powder of a complex oxide. The resulting complex oxide was then charged into an alumina plate, and annealed at a predetermined temperature of from 500 to 900°C for 2 hours. In this manner, lithium manganese complex oxides shown in Sample Nos. 1 to 26 in Table 1 were obtained. Note that the lithium manganese complex oxides of Sample Nos. 14 and 18 with asterisk are compounds for the invention.

A lithium manganese complex oxide of the formula $LiMn_2O_4$ shown in Sample No. 27 in Table 1 was obtained by a melt-impregnation method for comparison. That is, lithium nitrate and electrolytic manganese dioxide were first prepared as starting materials. Then, 1 mol of lithium nitrate and 2 mols of electrolytic manganese dioxide were accurately weighed, and milled and mixed using a ball mill. The mixture was then calcined at 700°C for 2 hours to obtain the complex oxide.

Table 1

Sample No.	Starting materials		$Li(Mn_{2-x}Li_x)O_4$	Atomizing temperature	annealing temperature
	lithium	manganese			
1	lithium nitrate	manganese nitrate	0	400	800
2	lithium nitrate	manganese nitrate	0	500	800
3	lithium nitrate	manganese nitrate	0	850	800
4	lithium nitrate	manganese nitrate	0	750	800
5	lithium nitrate	manganese nitrate	0.002	750	800
6	lithium nitrate	manganese nitrate	0.005	750	800
7	lithium nitrate	manganese nitrate	0.01	750	800
8	lithium nitrate	manganese nitrate	0.015	750	800
9	lithium nitrate	manganese nitrate	0.018	750	800
10	lithium nitrate	manganese nitrate	0.030	750	800
11	lithium nitrate	manganese nitrate	0.060	750	800
12	lithium nitrate	manganese nitrate	0.100	750	800
13	lithium nitrate	manganese nitrate	0	900	800
*14	lithium nitrate	manganese nitrate	0	700	500
15	lithium nitrate	manganese nitrate	0	700	600
16	lithium nitrate	manganese nitrate	0	700	800
17	lithium nitrate	manganese nitrate	0	700	850
*18	lithium nitrate	manganese nitrate	0	700	900
19	lithium acetate	manganese acetate	0	700	800
20	lithium formate	manganese formate	0	700	800
21	lithium nitrate	manganese formate	0	500	800
22	lithium nitrate	manganese formate	0	850	800
23	lithium nitrate	manganese formate	0	900	800
24	lithium nitrate	manganese formate	0	700	600
25	lithium nitrate	manganese formate	0	700	800
26	lithium nitrate	manganese formate	0	700	850
*27	lithium nitrate	electrolytic manganese dioxide	0	700 (Melt-impregnation method)	

Photographs of the above-obtained complex oxide powders were taken by means of a scanning electron microscope (SEM) to measure the particle diameters thereof. Further, the specific surface areas of the complex oxides were measured by a nitrogen adsorption method. Still further, the identification of the complex oxides was conducted by an X-ray diffraction (XRD) analysis. The results are shown in Table 2. In Table 2, LM is short for spinel-type lithium manganese complex oxide, and Mo is short for Mn_2O_3.

Table 2

Sample No.	Average particle diameter_@(micrometer)	Specific surface area (m^2/g)	XRD analysis Phase
1	1.8	2.1	LM, MO
2	1.7	2.7	LM
3	1.9	3.0	LM
4	2.4	3.5	LM
5	2.4	3.6	LM
6	2.3	3.6	LM
7	2.3	3.7	LM
8	2.2	3.6	LM
9	2.3	3.7	LM
10	2.5	3.6	LM
11	2.3	3.6	LM
12	2.7	3.0	LM
13	2.4	2.3	LM
*14	0.8	14.8	LM
15	1.6	8.4	LM
16	2.1	3.3	LM
17	1.9	2.5	LM
*18	5.5	0.5	LM
19	1.4	2.9	LM
20	2.1	2.8	LM
21	1.4	3.4	LM
22	1.9	3.5	LM
23	2.4	2.3	LM
24	1.8	4.6	LM
25	2.1	3.6	LM
26	1.9	2.6	LM
*27	3.4	1.8	LM

Secondary batteries were prepared using the above-mentioned complex oxides as cathode active materials.

That is, the powder of each above complex oxide, acetylene black as an electroconductive agent and polytetrafluoroethylene as a binder were kneaded, and the mixture was formed into a sheet. This sheet was pressed on an SUS mesh to obtain a cathode.

Subsequently, as shown in Fig. 1, the above-mentioned cathode 3 and a lithium metal as a anode 4 are overlaid through a polypropylene separator 5 with the SUS mesh side of the cathode 3 outside, and the product was stored in a stainless steel cathode can 1 with the cathode 3 down. The separator 5 was immersed with an electrolyte. A solution of lithium perchlorate in a mixed solvent of propylene carbonate and 1,1-dimethoxyethane was used as the electrolyte. Thereafter, an opening of a cathode can 1 was sealed with a stainless steel negative electrode 2 through an insulation packing to complete a lithium secondary battery shown in Table 2.

Then, the resulting lithium secondary battery was subjected to a charge-discharge test in 100 cycles under such conditions that a charge-discharge current density was 0.5 mA/cm^2, a charge limit voltage was 4.3 V and a discharge cut off voltage was 3.0 V. The secondary battery after the completion of the charge-discharge cycle test was then dis-

sembled, and the condition (presence or absence of peeling-off) of the cathode was visually observed. The results are shown in Table 3.

Table 3

Sample No.	Discharge volume		Peeling-off of a positive pole
	Initial	After 100 cycles	
1	86	65	No
2	128	126	No
3	130	127	No
4	133	122	No
5	131	124	No
6	130	126	No
7	130	128	No
8	129	126	No
9	128	125	No
10	122	118	No
11	115	112	No
12	96	95	No
13	136	132	No
*14	133	113	Yes
15	138	136	No
16	140	136	No
17	136	135	No
*18	102	98	No
19	128	125	No
20	129	125	No
21	127	125	No
22	129	126	No
23	135	131	No
24	137	135	No
25	139	135	No
26	135	134	No
*27	115	103	No

From the results in Tables 1 and 2, it is found that when the solution of the metallic elements constituting the lithium manganese complex oxide are atomized and pyrolyzed and then annealed, the complex oxide is obtained in which the average particle diameter is increased to between 1 and 5 mm and the specific surface area is adjusted to between 2 and 10 m^2/g. Further, this complex oxide is a spinel-type lithium manganese complex oxide. When this complex oxide is used as a cathode material, the lithium secondary battery is obtained which is excellent in the initial capacity and the charge-discharge cycle characteristics and which is free from peeling-off of the battery.

The specific pyrolyzing temperature is preferably between 500 and 900°C. When it is higher than 500°C, a single phase of a spinel-type lithium manganese complex oxide is obtained. The upper limit thereof is less than a temperature at which the spinel-type lithium manganese complex oxide is not pyrolyzed again.

The specific annealing temperature is preferably between 600 and 850°C. That is, at the annealing temperature of between 600 and 850°C, the spinel-type lithium manganese complex oxide having the particle size appropriate as a cathode active material of a lithium secondary battery can be obtained.

Upon comparison of Sample Nos. 4 to 12, when the amount x of substitution of manganese with lithium is $0 < x$ in the formula $Li(Mn_{2-x}Li_x)O_4$, the effect of controlling the Jahn-Teller phase transition is obtained, and the decrease in the capacity in the charge-discharge cycle is suppressed. Meanwhile, when the amount x of substitution is 0.10 or less, preferably less than 0.02, the higher initial capacity can be provided. Accordingly, x in the formula $Li(Mn_{2-x}Li_x)O_4$ is preferably $0 \leq x \leq 0.10$, preferably $0 < x < 0.02$.

In the above-mentioned Example, the compounds of the metallic elements constituting the complex oxide of the formula $Li(Mn_{2-x}Li_x)O_4$ were nitrates, acetates or formates. However, the present invention is not limited thereto. That is, compounds which are dissolved in water or alcohol, such as chlorides, can also be used as required.

Sample No. 25 in which lithium nitrate is used as a Li compound and magnesium formate as an Mn compound among the compounds of the metallic elements constituting the compound of the formula $Li(Mn_{2-x}Li_x)O_4$ exhibits the higher discharge capacity than Sample No. 19 in which lithium acetate and manganese acetate are used or Sample No. 20 in which lithium formate and manganese formate are used, and the discharge capacity of Sample No. 25 is as high as that of Sample No. 16 in which lithium nitrate and manganese nitrate are used. When using lithium nitrate and manganese formate, the reaction represented by formula (1) occurs, and the amount of NO_2 formed is one-fifth that of NO_2 when using lithium nitrate and manganese nitrate that cause the reaction represented by formula (2). Thus, it is easy to treat a waste gas after the reaction. Accordingly, it is most preferable to use lithium nitrate and manganese formate as compounds of metallic elements constituting the complex oxide of the formula $Li(Mn_{2-x}Li_x)O_4$.

$$LiNO_3 + 2Mn(HCOO)_2 + 2.5O_2 \rightarrow LiMn_2O_4 + 4CO_2 + NO_2 + 2H_2O \quad (1)$$

$$LiNO_3 + 2Mn(NO_3)_2 \rightarrow LiMn_2O_4 + 5NO_2 + 0.5O_2 \quad (2)$$

When the spinel-type lithium manganese complex oxide is a compound oxide obtained by substituting a part of an Mn site of $Li(Mn_{2-x}Li_x)O_4$ with Cr, Ni, Fe, Co or Mg, other than $Li(Mn_{2-x}Li_x)O_4$, the same effects can also be obtained.

Claims

1. A spinel-type lithium manganese complex oxide for a cathode active material of a lithium secondary battery, characterized in that
said spinel-type lithium manganese complex oxide has an average particle diameter between 1 and 5 micrometers and a specific surface area between 2 and 10 m^2/g.

2. A spinel-type lithium manganese complex oxide according to Claim 1, characterized in that
said spinel-type lithium manganese complex oxide is represented by the formula $Li(Mn_{2-x}Li_x)O_4$ wherein x is $0 \leq x \leq 0.1$.

3. A spinel-type lithium manganese complex oxide according to Claim 1, characterized in that
said spinel-type lithium manganese complex oxide is represented by the formula $Li(Mn_{2-x}Li_x)O_4$ wherein x is $0 < x < 0.02$.

4. A spinel-type lithium manganese complex oxide according to Claim 1, characterized in that
said spinel-type lithium manganese complex oxide is represented by the formula $Li(Mn_{2-x}Li_x)O_4$ wherein x is $0 \leq x \leq 0.1$, and Mn is partially substituted by Cr, Ni, Fe, Co, or Mg.

5. A spinel-type lithium manganese complex oxide according to Claim 1, characterized in that
said spinel-type lithium manganese complex oxide is represented by the formula $Li(Mn_{2-x}Li_x)O_4$ wherein x is $0 < x < 0.02$, and Mn is partially substituted by Cr, Ni, Fe, Co, or Mg.

6. A process for producing the spinel-type lithium manganese complex oxide according to one of Claims 1 to 5, comprises the steps of:

1)atomizing and pyrolyzing at least one of an aqueous solution and an alcohol solution of compounds containing metallic elements constituting a spinel-type lithium manganese complex oxide to obtain said compound oxide, and

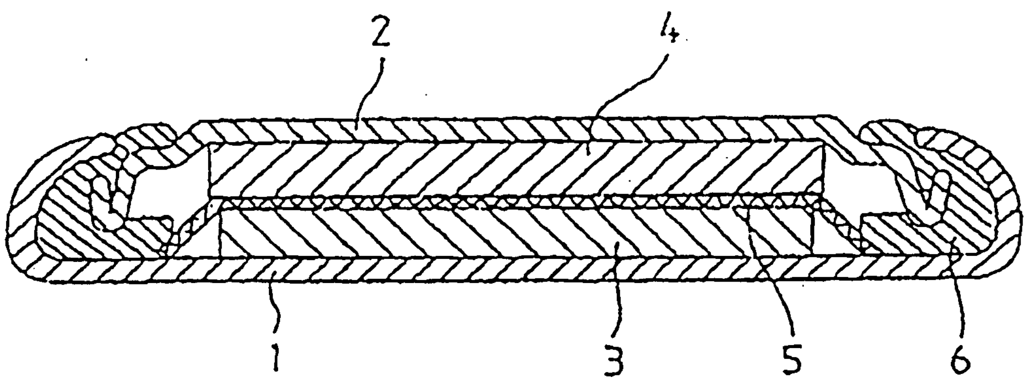
2)annealing said spinel-type lithium manganese complex oxide to increase the average particle diameter thereof to between 1 and 5 micrometers and adjust the specific surface area thereof to between 2 and 10 m^2/g.

7. The process according to Claim 6,
characterized in that
the atomizing and pyrolyzing temperature is between 500 and 900°C.

8. The process according to Claim 6 or 7,
characterized in that
the annealing temperature is between 600 and 850°C.

9. The process according to one of Claims 6 to 8,
characterized in that
said compounds containing the metallic elements are at least one of lithium nitrate, lithium acetate and lithium formate and at least one of manganese nitrate, manganese acetate and manganese formate.

Fig. 1



European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 10 9043

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	MANEV V ET AL: "SYNTHESIS OF LIMN2O4 FOR RECHARGEABLE LITHIUM-ION BATTERY" PROGRESS IN BATTERIES & BATTERY MATERIALS, vol. 14, pages 101-124, XP000590058 * page 107, paragraph 3 * * page 110, paragraph 2 * ---	1	H01M4/50 C01G45/02
A	GB 2 221 213 A (CSIR) 31 January 1990 * table, controls 5 and 6 * * page 1, line 21 - page 2, line 4; claims 1,2 * * page 10, line 14 * ---	1,2,6,9	
A	PISTOIA G ET AL: "SYNTHESIS OF AN EFFICIENT LIMN2O4 FOR LITHIUM-ION CELLS" JOURNAL OF POWER SOURCES, vol. 58, no. 2, pages 135-138, XP000631998 * page 137, line 26 - line 29 * * page 138, line 12 - line 15 * ---	1,2	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
A	EP 0 413 313 A (SANYO ELECTRIC CO) 20 February 1991 * page 5, line 17 - line 19; claim 1; tables 1,2 * * page 9, line 46 - line 49 * ---	1	H01M C01G
A	EP 0 390 185 A (MATSUSHITA ELECTRIC IND CO LTD) * claim 1 * ---	4	
A	WO 92 18425 A (BELL COMMUNICATIONS RES) * page 5, line 6 - line 19; claim 1 * --- -/--	6,8,9	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	21 October 1997	Andrews, M

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 10 9043

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP 0 651 450 A (FUJI PHOTO FILM CO LTD) * page 39, line 31 - line 33; claims 15,17,18 * * page 10, line 2 - line 22 * -----	1,2,4	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	21 October 1997	Andrews, M

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)